

# Electrolyte gate dependent high-frequency measurement of graphene field-effect transistor for sensing applications

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## Abstract

We performed radiofrequency (RF) reflectometry measurements at 2–4 GHz on electrolyte-gated graphene field-effect transistors (GFETs) utilizing a tunable stub-matching circuit for impedance matching. We demonstrate that the gate voltage dependent RF resistivity of graphene can be deduced even in the presence of the electrolyte which is in direct contact with the graphene layer. The RF resistivity is found to be consistent with its DC counterpart in the full gate voltage range. Furthermore, in order to access the potential of high-frequency sensing for applications, we demonstrate time-dependent gating in solution with nanosecond time resolution.

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Owing to its atomically thin structure and exceptional high mobilities,<sup>1-3</sup> graphene is potentially well suited to radiofrequency (RF) applications. This prospect is reinforced by the relative openness of the RF-electronics industry to new materials without the requirement of a high on/off current ratio, which limits the application of graphene for digital applications.<sup>4</sup> Much of the research conducted so far on graphene RF transistors has focused on the cut-off frequency,  $f_T$ , which is the highest frequency at which a field-effect transistor (FET) is useful in RF applications.<sup>5-10</sup> For instance, graphene FETs (GFETs) with an intrinsic cut-off frequency of  $f_T = 100 - 300$  GHz have been demonstrated,<sup>6,8</sup> which are superior to the best silicon MOSFETs with similar gate lengths. Graphene full-wave rectification and consequently frequency conversion with high efficiency have also been demonstrated by making use of the ambipolar conduction properties.<sup>11,12</sup> The cyclotron motion of the charge carriers of graphene in a magnetic field suggests further applications in non-reciprocal components.<sup>13,14</sup> Moreover, the microwave properties of graphene antennas and transmission line have also been investigated.<sup>15,16</sup>

Recently, there is also growing interest in applying graphene RF transistors to biochemical sensing applications.<sup>17,18</sup> But in spite of the rapid advances in recent years, our understanding of the RF properties of graphene, especially with regards to sensing in a liquid environment, is still incomplete. Although it is known that atomically thin large area graphene behaves as a wideband resistor due to negligible skin effect and kinetic inductance,<sup>19</sup> it is difficult to measure the device resistance directly at RF. This is due to the large shunt capacitance in conventional back or top-gated graphene RF transistors having a significant influence on the RF performance, hindering (if not preventing) the extraction of the intrinsic parameters of graphene.

In contrast to conventional oxide based back or top gating, electrolyte gating can be used to tune the properties of GFETs without shunting the propagating RF signal. This is because of the unique frequency dependent properties of the electrolyte. At DC and relatively low frequency  $\lesssim 10$  MHz the ions in the electrolyte can instantly respond to potential changes. Due to ideal screening, an electrode in the electrolyte, even if placed far away from the graphene surface, is very strongly coupled to the graphene layer and therefore able to induce large changes in the carrier concentration in graphene. The typical Debye screening length in an ionic buffer solution at a concentration of 100 mM is as small as 1 nm. In contrast, at high frequency  $> 100$  MHz the ions in the electrolyte start to lag behind the

AC electric field due to the viscosity of the solution.<sup>21</sup> As a result, the electrolyte behaves as a pure dielectric at microwave frequency and the RF shunt gate capacitance is negligible considering that the physical gate electrode in the electrolyte can be placed far away from the graphene samples.

In this work, we explore the RF properties of electrolyte-gated GFETs by using an RF reflectometry technique. We demonstrated that it is possible to deduce the gate dependent RF resistivity of graphene at microwave frequencies by modeling the graphene sheet as an  $RC$  dissipative transmission line. The extracted RF resistivity of graphene is found to be consistent with its DC counterparts in the full gate voltage range. As a proof-of-principle for high-speed sensing applications in liquids, we demonstrate in addition nanosecond time-resolved measurements in electrolytes. We believe that this work opens the avenue for further research on a new generation of biochemical sensors. For example, owing to its wide bandwidth and significantly reduced  $1/f$  noise at high frequencies, our graphene RF device will enable ultrafast measurements with a good detection limit, allowing to explore new phenomena and physics at the solid-liquid interface.

In reflectometry the intensity of the reflected wave of an RF signal is measured relative to the input signal yielding the frequency dependent reflection coefficient  $S_{11}$ . This value depends on the load impedance. The sensitivity to the load is optimized if the load impedance matches the characteristic impedance of the transmission line at  $50\ \Omega$ . In our graphene devices, typical resistances are in the range of  $1 - 100\ \text{k}\Omega$ , which is far off the matching value of the transmission line. To achieve a better signal, we use the recently developed approach<sup>22,23</sup> based on stub-matching<sup>24</sup>. Here, a stub is added to the waveguide to realize an impedance matching circuit that converts the large impedance of the graphene devices to a value close to  $50\ \Omega$ . The stub-matching circuit is realized on a printed circuit board (PCB, RO4003C) with coplanar waveguides (CPWs) and ground planes made from a  $40\ \mu\text{m}$  Cu film with an additional  $3 - 6\ \mu\text{m}$  Ni/ $0.1\ \mu\text{m}$  Au plating and integrated with the graphene sample, see Fig. 1. Reflectometry measurements are performed with a vector network analyzer (VNA) connected via a bias tee to the PCB. The bias tee is needed for DC measurements. All the components are placed at room temperature. Impedance matching is achieved by shunting the CPW connecting to the graphene sample by a stub placed at a distance of  $d_1$  from the sample (Fig. 1b). The stub itself is a CPW with a length  $d_2$  and is terminated by a varactor diode. The capacitance  $C_d$  of the diode can be tuned by applying a DC voltage  $V_d$

through an additional on-chip bias tee as depicted in Fig. 1a and 1b (dashed red circle). To achieve impedance matching, both  $d_1$  and  $d_2$  have to be chosen close to  $\lambda/4$ , where  $\lambda$  is the wavelength of the 3 GHz carrier signal. The reflectometry setup is first calibrated up to the input of the PCB using standard procedures and commercial calibration kits. To calibrate the PCB board, frequency dependent measurements were performed with and without the graphene device.

Fig. 1c show the reflection coefficient  $S_{11}$  versus frequency  $f$  at different diode voltages  $V_d$  without a graphene device. First, by tuning the capacitance  $C_d$  of the diode, the best matching is achieved at around 3 GHz with  $V_d = 8.72$  V (green line, Fig. 1c) where  $S_{11}$  is lower than  $-60$  dB. At this resonant point at matching we measure a full width at half maximum of around 100 MHz, which places an upper limit on the setup bandwidth. Second, by fitting the frequency-dependent  $S_{11}$  curves using previously described calibration methods and models,<sup>22,23</sup> we are able to extract the electrical lengths of  $d_1 = 13.92$  mm and  $d_2 = 14.12$  mm, values that are close to the design values  $d_1 = 13.45$  mm and  $d_2 = 13.75$  mm. The extracted attenuation constant of the CPW on the PCB is found to be  $\alpha = 5.15$  dB/m at a frequency of 3 GHz, which is comparable to  $\alpha \sim 4.6$  dB/m obtained from simulations of the PCB board (TXLINE 2003). After this calibration measurements, the graphene sample is glued into an  $8 \times 8$  mm<sup>2</sup> recess at the end of the  $d_1$  CPW and connected with several bonding wires at both sides. There are bonds from the  $d_1$  stub to the graphene and on the opposite side a series of bonds to the ground plane. The graphene sample together with the bonding wires is then further encapsulated to allow for measurements in a liquid environment.

Previously, we have demonstrated that high-mobility GFETs with clean surfaces, and thus preserved chemical properties, can be fabricated using large-scale chemical vapor deposition (CVD).<sup>25,26</sup> These transistors can serve as an ideal platform for biochemical sensing applications. In this study, we explore the microwave properties of such GFETs. As shown in Fig. 2a, we start with large area CVD graphene synthesized on Cu.<sup>25-27</sup> Then a uniform layer of epoxy is put on a teflon substrate and a piece of graphene on copper is carefully placed over it upside down. The graphene flake is in direct contact with epoxy and on the opposite side the copper layer faces air. The edges of the Cu surface are then manually covered with PMMA as an easy way to obtain source and drain electrodes after etching the Cu film in the middle. Due to the good adhesion of the graphene flake on epoxy, the exposed Cu can be etched away in an ammonium persulfate solution leaving the intact graphene un-

derneath. Afterwards, the PMMA can be carefully peeled away to release the Cu electrodes. Such fabricated GFETs on teflon substrates are placed at the end of the stub tuner and connected with wire bonds. At the end of fabrication, an additional epoxy step is applied to seal the Cu electrodes as well as the bonding wires from liquid.

Fig. 2b shows the schematics and measurement circuits of such a GFET device. The electrostatic potential in the electrolyte is defined via a calomel reference electrode. This potential is gating the graphene sample. Fig. 2c shows the dependence of the measured DC electrical resistance  $R$  of a GFET as a function of the gate voltage applied to the calomel reference electrode  $V_{ref}$  (pink circle: forward, black star: backward sweep) in a 100 mM KCl solution. Negligible hysteresis can be identified in this transfer characteristics. This is an indication of the reliability and reproducibility of the device and the measurements.

After evaluating the DC transfer characteristics of the electrolyte-gated GFET, we measured its frequency dependent reflection coefficient  $S_{11}$  when sweeping the liquid gate voltage  $V_{ref}$  from  $-0.7$  V to  $0.1$  V in steps of  $0.1$  V in 100 mM KCl solution. For reasons of clarity, Fig. 3a shows only a few curves measured at  $-0.7$  V (green dots),  $-0.2$  V (black dots), and  $0.1$  V (blue dots). In order to fit the measured curves, we introduce an  $RC$  dissipative transmission line model. This model treats the graphene sheet as a distributed  $RC$  line along which the RF signal propagates. We thereby neglect the graphene inductance which yields a negligible contribution to the impedance in our frequency range.<sup>19</sup> Fig. 3a (inset) depicts such a circuit. Here,  $R'$  represents the resistance of graphene and  $C'$  the shunt capacitance both normalized per unit length. An RF wave propagating along the  $RC$  transmission line is damped due the resistive component. At a distance  $x$ , the amplitude of the RF signal will decrease by a factor of  $\exp[-\sqrt{\omega R' C' / 2} x]$ , where  $\omega$  is the angular frequency. The characteristic propagation length over which the signal decays by a factor of  $1/e$  is then given by  $L_\lambda = \sqrt{2 / \omega R' C'}$ . The capacitance per unit length  $C'$  is determined by the dielectric materials leading to ground. As the ions in the liquid cannot follow the RF field at 3 GHz the main part of the capacitance is given by the substrate, and since the substrate capacitance is much smaller than the quantum capacitance  $C_Q$ ,<sup>28</sup> the latter does not play a role at RF frequencies. In order to keep this capacitance low enough we have chosen to work with teflon as a substrate material, hence,  $C' = \epsilon_o \epsilon_{teflon} W / d$ , with  $d = 1$  mm the thickness of the teflon substrate and  $W = 2.4$  mm the width of the graphene sheet. The water solution (electrolyte) on the upper surface yields only a secondary contribution to  $C'$  which is then

captured in the fitting by a slight increase in the effective dielectric constant relative to the published value of  $\varepsilon_{teflon}$ .

Having established a calibration up to the open end of the CPW, we need to also measure the contact resistance  $R_s$  and stray capacitance  $C_s$  of the bonding wires including the bonding pads. These values are obtained by fitting similar curves as in Fig. 3a after removal of the graphene in an  $O_2$  plasma. Consequently, there are only two fitting parameters for each curve in Fig. 3,  $C'$  and  $R'$ .  $C'$  is related to an effective dielectric constant, while we convert  $R'$  into a sheet resistance or resistivity  $\rho$  given by  $\rho = R'w$ . The result of the fitting is shown in Fig. 3a as dashed curves. It turns out that all curves can be fitted with the same capacitance value  $C'$ . The extracted effective  $\varepsilon_{teflon} = 2.4$  is found to be close to the reported dielectric constant of teflon which is 2.1. This strongly supports the proposed model. We stress here that this finding was reached by measurements carried out in both air and liquid environments at different salt concentrations and pH values (not shown).

The gate-dependent resistivity values  $\rho_{RF}$  deduced from the  $S_{11}$  measurements are shown together with the DC measurements  $\rho_{DC}$  in Fig. 3b. As can be seen, there is a perfect match between  $\rho_{RF}$  and  $\rho_{DC}$ . This is in agreement with the notion that the skin effect is negligible in ultra thin monolayer graphene.<sup>16,19</sup> The graphene RF resistivity  $\rho_{RF}$  ranges between 1 and 5 k $\Omega$ , yielding a range of 0.4 to 2 k $\Omega$ /mm for  $R'$ . The shunting capacitance per area  $C_{\square} = \varepsilon_o \varepsilon_{teflon} / d \sim 2 \times 10^{-8}$  F/m<sup>2</sup> yields  $C' = 0.5$  aF/mm. This predicts a propagation length  $L_{\lambda} \sim 1 - 2.3$  mm at 3 GHz, which is rather short. When the graphene sheet is longer than 1 mm, which is the case in the above device, the RF wave cannot propagate to the end, but most of the signal is dissipated before. We therefore stress that it is important to use a transmission line model and not only a fixed two-terminal graphene resistance. The latter parameter can be measured at low frequency. At high frequency the the resistivity is the more natural physical quantity.

Having demonstrated the ability to measure the gate-dependence of the graphene resistivity in an electrolyte, one may wonder how large the attainable measurement bandwidth is. We therefore performed time resolved measurements on the electrolyte-gated GFETs. The used homodyne measurement setup is sketched in Fig. 4a. A square wave at 2 MHz with a rise time of 7 ns is generated by a pulse generator and applied to the electrolyte gate of the GFET via a Au wire. The peak-to-peak voltage of the square wave is 200 mV and its low level is adjusted to the  $V_{CNP}$  of the GFET. At the same time, a -30 dBm RF

carrier signal (here at 3.55 GHz) is applied to the input of the stub tuner/GFET device via a directional coupler ( $-20$  dB coupling). The resulting reflected signal exits the output port of the directional coupler and is down-converted to DC using a mixer with the carrier signal as local oscillator. Afterwards the signal is low pass filtered, amplified and recorded by an oscilloscope at a sampling rate of 1 GHz. Fig. 4b depicts the reference square wave (applied to the electrolyte gate via a Au wire) and the collected reflected signals for different KCl concentrations ranging from 1 mM to 1 M. We measure a rise time of  $t_{rise} = 50$  ns in KCl solution for both 100 mM and 1 M concentrations. In contrast, in case of the 10 mM KCl solution the reflected signal starts to show a significant delay compared to the 2 MHz square wave. At even lower concentration of 1 mM concentration, the reflected signal is small and cannot build up on this time scale. Additional measurements reveal rise times of about  $0.4 \mu\text{s}$  and  $4 \mu\text{s}$  for a 10 mM and a 1 mM concentrated solutions.

The rise time is plotted in the inset of Fig. 4b as a function of ion concentration  $c$ . It can be quantitatively explained by looking into the equivalent  $RC$  circuits of the electrolyte-gated GFETs, which consists of the interfacial capacitance  $C_I$  and the series resistances to which both the water solution and graphene device contribute. First, the DC (or low frequency) interfacial capacitance  $C_I$  of an electrolyte-gated GFET can be modeled as two capacitors in series.<sup>26,28</sup> One part is the quantum capacitance of graphene,  $C_Q$ , which is gate voltage dependent and has its minimum value at the charge neutral point (CNP). The other part is the double layer capacitance,  $C_{DL}$ , which is independent to the gate voltage. Here, in our case of moderate to high ionic strength (from 1 mM to 1 M), the double layer capacitance  $C_{DL}$  is limited by the Stern layer capacitance  $C_{Stern}$  which is on the order of  $0.2 \text{ F/m}^2$ . This number is over one order of magnitude larger than the quantum capacitance of graphene  $C_Q \sim 0.01 \text{ F/m}^2$  near the CNP at low carrier density. Hence,  $C_Q$  dominates the interface capacitance in the low frequency regime.<sup>26,28</sup> Secondly, the resistance between the water solution and the graphene flake is inversely proportional to the KCl concentration,  $R_W \propto 1/c$ . It can be estimated to be about  $10 \text{ k}\Omega$  to  $10 \text{ M}\Omega$  for KCl concentrations in the range of 1 mM to 1 M. As a comparison, the resistance of our graphene flake is of the order of  $\text{k}\Omega$ . This is up four to orders of magnitude lower than that of the water solution  $R_W$ . Based on this discussion, the time constant of the system can be estimated as  $\tau = R_W C_Q \propto 1/c$ . This trend satisfactorily explains the observed KCl concentration dependent rise times of the electrolyte-gated GFET system seen in the inset of Fig. 4 (grey line). A saturation of the time scale occurs at  $\sim 50$  ns

for large ion concentrations. This is an extrinsic effect mainly caused by the amplifier which (only) had a 10 MHz bandwidth, limiting the response to 35 ns. The linear dependence shows, however, that a 10 ns response time is feasible in a highly concentrated buffer solution as used in biological studies. This time scale would then also approach the bandwidth limit of the impedance matching circuit. The presented measurements demonstrate the feasibility of achieving nanosecond time resolution in measurements of the electrostatic potentials at the electrolyte graphene surface.

In conclusion, this work represents a systematic study of the gate voltage dependent characterization of large scale monolayer CVD GFET at microwave frequencies in a liquid environment. Using the reflectometry technique, we measured the frequency dependent reflection coefficient  $S_{11}$  at different electrolyte gate voltages. An  $RC$  dissipative transmission line model is proposed to extract the RF resistivity of GFETs after de-embedding, which is found to follow its DC counterparts. The tunable transmission lines realized by using high-mobility liquid-gated GFETs can serve as a platform for a new generation of biochemical sensors. Potentially, the wide bandwidth (100 MHz) offered by this high-frequency measurements enables ultra fast measurements in liquid with 10 ns time resolution.

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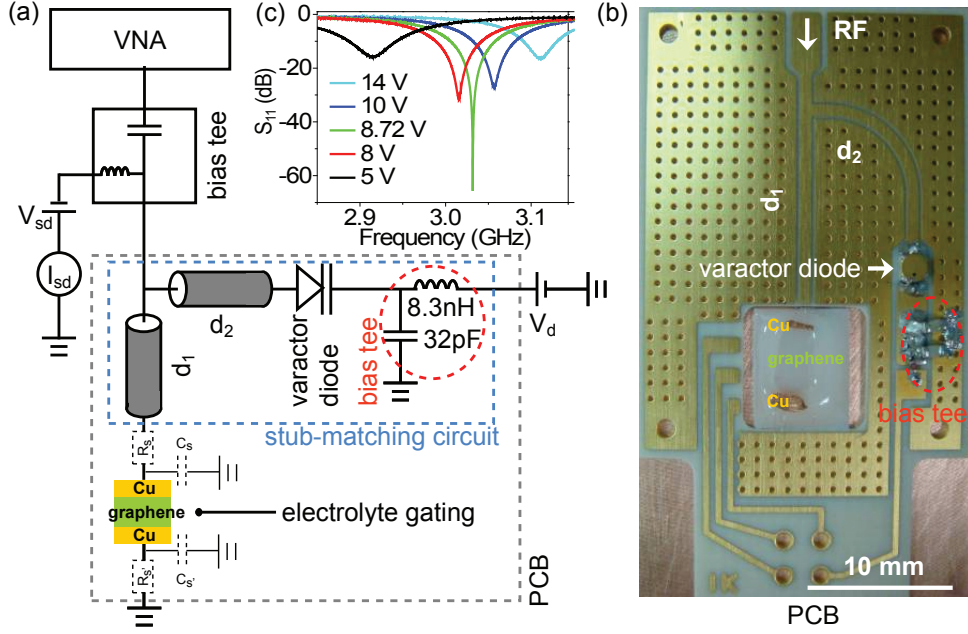


FIG. 1: (a) Experimental setup used to perform the reflectometry measurements at carrier frequencies of 2-4 GHz. (b) A picture of the PCB with a terminated waveguide ( $d_1$ ) and a shunted stub ( $d_2$ ). The graphene sample is connected to the  $d_1$  waveguide via wire bonding and  $d_2$  stub is terminated by a varactor diode, after which two capacitors and one inductor are placed as on-chip bias tee. (c) Open loop reflection coefficient  $S_{11}$  as a function of the carrier frequency  $f$  measured under different varactor diode bias voltages  $V_d$ .

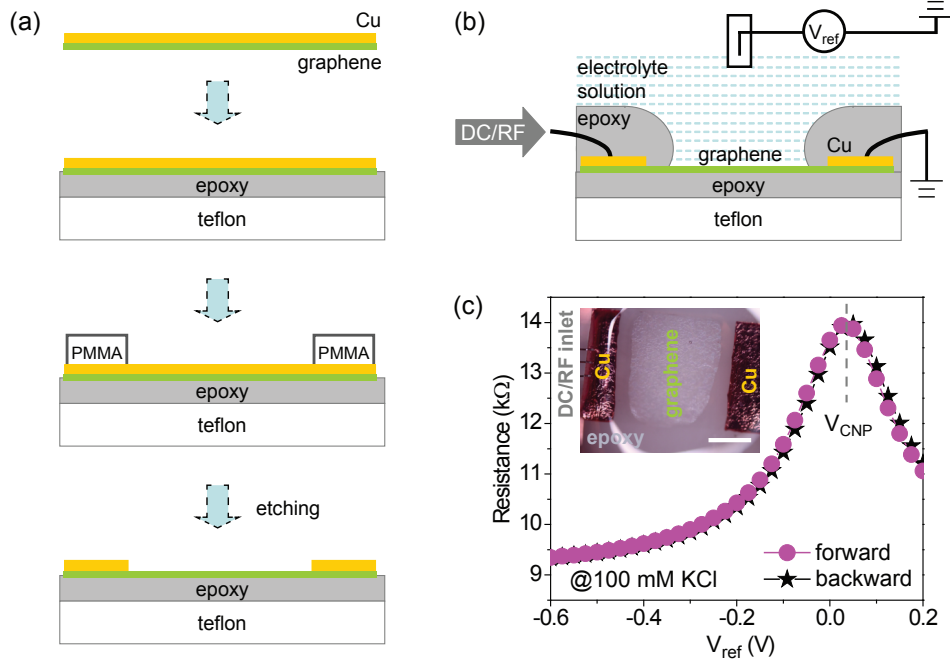


FIG. 2: GFET fabrication and measurement scheme. (a) Process flow for transferring and patterning a CVD graphene sheet (green) with clean surface. (b) Schematic of a fabricated GFET with liquid sealing and the electrical circuitry of the electrolyte-gated GFET. The electrostatic potential in the solution was defined by a commercial calomel reference electrode as  $V_{ref}$  or by a Au wire. (c) Electrical resistance of a GFET as a function of the reference potential  $V_{ref}$  measured in 100 mM KCl solution with negligible hysteresis. Inset, an optical image of the GFET under test. Scale bar: 1 mm.

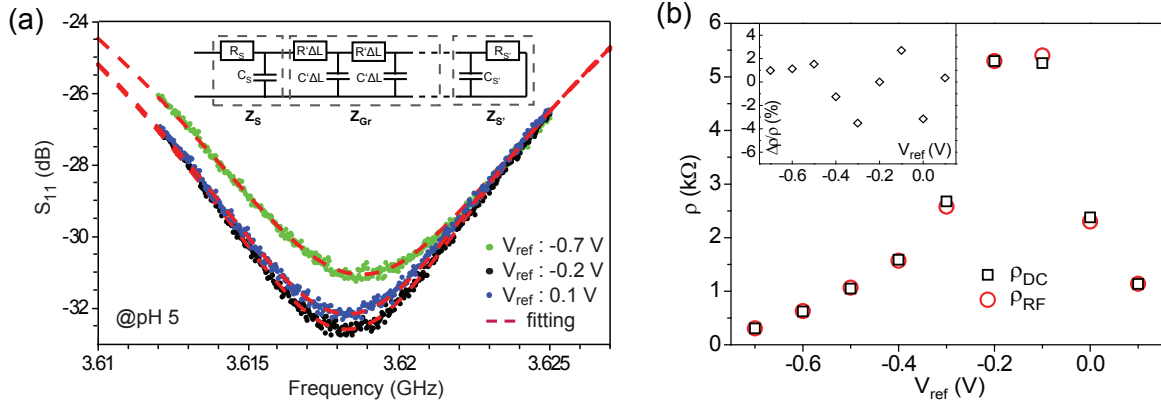


FIG. 3: (a) The measured reflection spectra at different liquid gate voltages  $V_{ref}$  and the corresponding fitting curves. Inset: the  $RC$  dissipative transmission line model. (b) The measured DC resistivity  $\rho_{DC}$  (black squares) and the extracted small-signal RF resistance  $\rho_{RF}$  (red circles) as a function of the applied liquid gate voltage  $V_{ref}$ . Inset: the relative deviation between  $\rho_{DC}$  and  $\rho_{RF}$  ( $\Delta\rho/\rho := (\rho_{RF} - \rho_{DC})/\rho_{DC} \times 100\%$ ) as a function of the applied liquid gate voltage  $V_{ref}$ .

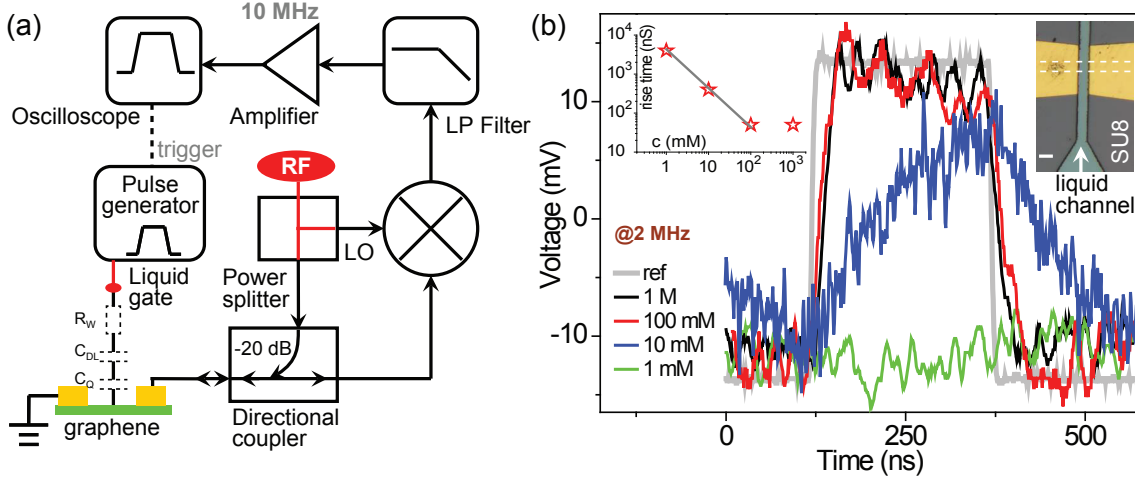


FIG. 4: (a) Schematic of the time-resolved homodyne measurement setup. (b) Sensing responses of the GFET to a 500 ns square wave reference signal with 200 mV peak-to-peak voltage applied to the liquid gate (normalized, grey line), in KCl solutions with concentration of 1 mM (green line), 10 mM (blue line), 100 mM (red line) and 1 M (black line). Inset, to the right: an optical image of the GFET with SU-8 (a photoresist) liquid sealing. The dashed white line is an indication of the graphene ribbon. Scale bar: 10  $\mu$ m. To the left: measured rise times as a function of the KCl concentration  $c$ . The grey line indicates a linear  $1/c$  behavior.